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EFFECT OF HYDROGEN ON WORK HARDENING OF  
TYPE 304L AUSTENITIC STAINLESS STEEL

by

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TYPE 304L AUSTENITIC STAINLESS STEEL\***

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**ABSTRACT**

The grain size and strain dependence of work hardening in Type 304L stainless steel were analyzed between 200 and 250 K where hydrogen damage is greatest. Tensile data were obtained for specimens of several grain sizes, both with and without prior exposure to hydrogen gas at 69 MPa pressure. The analysis suggests that hydrogen has little influence on lattice friction stress but has a large effect on dislocation interaction and the back stress of dislocation pileups.

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## INTRODUCTION

Hydrogen damage studies of Type 304L austenitic stainless steel over the past several years have emphasized fracture properties.<sup>1,2</sup> In past studies, flow stress was observed to increase if hydrogen were dissolved in the alloy.<sup>2</sup> The present study examines the grain size dependence of flow stress at temperatures of 200 to 250 K where hydrogen damage in Type 304L austenitic stainless steel is greatest.<sup>3</sup>

## EXPERIMENTAL DETAILS

Smooth-bar tensile specimens with a 4.8-mm diameter and a 25-mm-gage length were machined from the bar stock of a single heat of consumable electrode, vacuum-melted steel (Table 1). The average grain size of this steel was American Society for Testing Material (ASTM)  $11.4 \pm 0.25$  ( $6.4 \pm 0.2 \mu\text{m}$ ). Grain size was estimated according to the ASTM method of estimating grain size of metal (E112-77), except that both twin and grain boundaries were counted. Coherent twin boundaries were included because they have many properties in common with grain boundaries, such as acting as barriers to dislocation motion and dislocation sources during deformation.<sup>4</sup> Specimens with ASTM grain sizes of about 7 ( $26 \mu\text{m}$ ), about 6 ( $50 \mu\text{m}$ ), and 1 ( $300 \mu\text{m}$ ) were obtained by vacuum annealing for 24 hours at 1170, 1270, and 1470 K, respectively.

The tensile specimens were saturated with hydrogen when exposed to deuterium gas at 620 K for three weeks at a pressure of 69 MPa. Deuterium concentrations of the specimens analyzed with a LECO<sup>™</sup> model RH-1 Hydrogen Determinator (Leco Corp., St. Joseph, MI) averaged 4.7-cc D<sub>2</sub>/cc alloy (54 wt. ppm).

Specimens were broken in tension at a constant crosshead speed of 0.0085 mm/sec. The test temperature was 200 to 240 K, which was within the region of maximum hydrogen damage for Type 304L stainless steel. Stress-strain curves are shown in Figure 1a for specimens without any hydrogen exposure and in Figure 1b for specimens exposed to 69 MPa hydrogen. Plastic deformation of Type 304L stainless steel was strongly influenced by the planar slip mode and the formation of strain-induced martensite at these temperatures. The stress-strain curves are not linear on a log-log plot because of the martensite transformation which becomes detectable at a strain of 0.05. Furthermore, because exposure to hydrogen prior to testing suppresses the strain-induced transformation to martensite at the indicated test temperature, the stress-strain curves of the hydrogen-saturated specimens (Figure 1b) differ slightly in shape from the stress-strain curves with no hydrogen<sup>5</sup> (Figure 1a).

#### ANALYSIS OF WORK HARDENING

The grain size dependence of the flow stress ( $\sigma_f$ ) was analyzed by the Hall-Petch relation  $\sigma_f = \sigma_0 + k_f d^{-1/2}$

where  $\sigma_0$  and  $k_f$  were constants, and  $d$  was the grain diameter. Hall-Petch plots were made for several values of plastic strain from  $\epsilon_p = 0.01$  to 0.20. Representative plots are shown in Figure 2 for strains of 0.05 and 0.10. The grain size dependence of  $\sigma_f$  was small as observed in other alloys with a face-centered cubic lattice.<sup>6</sup> Furthermore, both  $\sigma_0$  and  $k_f$  were functions of strain.

Hydrogen dissolved in the specimens increased the grain size dependence of the flow stress. However, when specimens that did not contain dissolved hydrogen were tested in a high-pressure hydrogen environment, the grain size dependence of the flow stress was unchanged (Figure 3). This contrast in behavior between internal and external hydrogen sources indicated that external hydrogen damage was related to surface or near-surface processes only as suggested by other studies.<sup>7</sup>

The constants  $\sigma_0$  and  $k_f$  were further analyzed by a technique proposed by Meakin and Petch.<sup>8</sup> As seen in Figures 4a and 4b,  $\sigma_0$  varied linearly with strain, whereas  $k_f$  had a parabolic strain dependence up to a strain of 0.07 with no hydrogen and a strain dependence of 0.04 with hydrogen. The strain dependence of  $\sigma_0$  may be written  $\sigma_0 = \sigma_0' + a\epsilon$  where  $\sigma_0'$  and  $a$  (work hardening rate) are new constants dependent on the hydrogen content of the alloy. As seen in Table 2, hydrogen at a level of about 5 cc  $H_2$ /cc alloy increased  $\sigma_0$  but decreased  $a$ . Thus, a small

increase occurred in lattice friction associated with the interstitial hydrogen. Linear strain hardening of  $\sigma_0$  continued to a strain of 0.2, the largest strain that was analyzed.

The strain hardening contribution of  $k_f$  was parabolic to strains of around 0.04 to 0.07. This dependence may be expressed as  $k_f = k_f' + b\epsilon^{1/2}$ . The constant  $k_f'$  was decreased about 50% by hydrogen, and the constant  $b$  was increased by a factor of nine (Table 2). The major effect of hydrogen on work hardening, as reflected in the large change in  $b$ , appears to be associated with dislocation interactions in the grain boundary regions.<sup>6</sup> The effect of hydrogen on lattice friction was secondary.

The planar slip mode in Type 304L stainless steel was clearly reflected at low strain  $\epsilon_p < 0.05$  where  $k_f$  has a parabolic dependence on strain. Similar behavior was reported for alpha brass<sup>8</sup> and Type 330 stainless steel,<sup>9</sup> alloys which also had low-stacking fault energies.

The parabolic strain hardening term was explained by an average slip distance comparable to the grain size and work hardening by dislocation intersection.<sup>8</sup> This latter process is responsible for the break in the parabolic strain dependence of  $k_f$ . In the present case, strain-induced martensite formation begins at a strain of about 0.05<sup>5</sup> and may also contribute to reduction in  $k_f$  with further strain.

15

Evidence from analysis of grain size dependence of flow stress in Type 304L stainless steel indicates that the back stress of dislocation pileups controls work hardening rather than the forward stress across grain boundaries. Furthermore, hydrogen renders dislocation intersection substantially more difficult, an effect that may arise from hydrogen trapped in the dislocation stress fields.

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TABLE 1

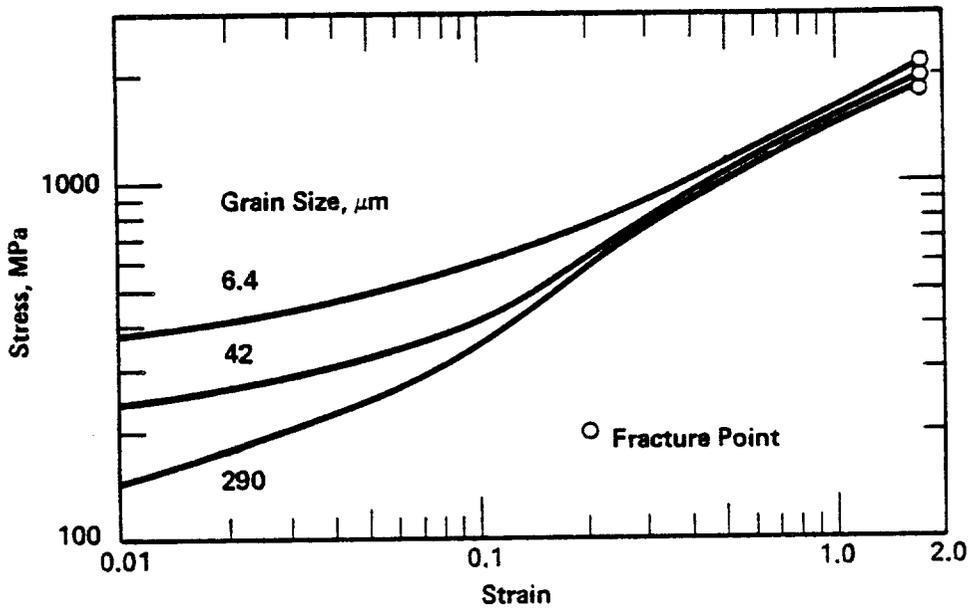
Type 304L Stainless Steel  
Chemical Composition, wt %

<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Cr</u>	<u>Ni</u>	<u>Mo</u>
0.03	1.57	0.015	0.008	0.43	18.35	10.29	0.17

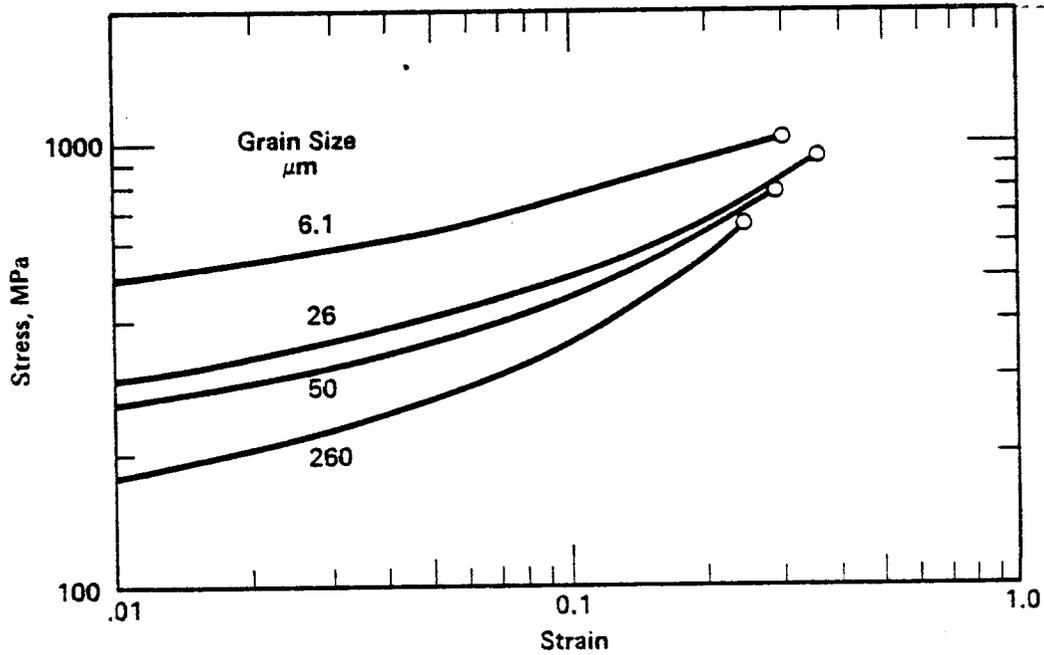
TABLE 2

Hall-Petch Parameters

Exposure	$\sigma_o$	a, MPa/strain	$k_f$	
	$\sigma_o'$ , MPa		$k_f'$ MPa $\sqrt{\mu\text{m}}$	b, MPa $\sqrt{\mu\text{m}/\sqrt{\text{strain}}}$
None	78	2370	660	360
69 MPa H <sub>2</sub>	106	1860	430	3330



1a. No Hydrogen Exposure



1b. Specimens Exposed to Hydrogen at 69 MPa Pressure.

FIGURE 1. True Stress - Natural Strain Curves in Type 304L Stainless Steel

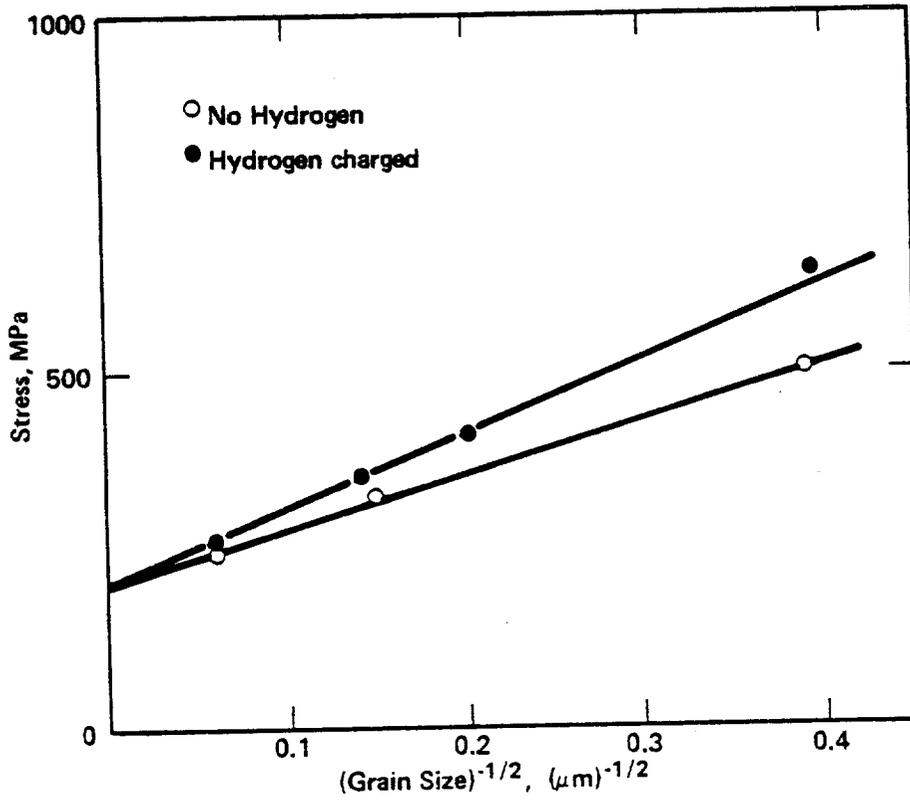


FIGURE 2. Hall-Petch Plot of Flow Stress at 0.05 Plastic-Strain.

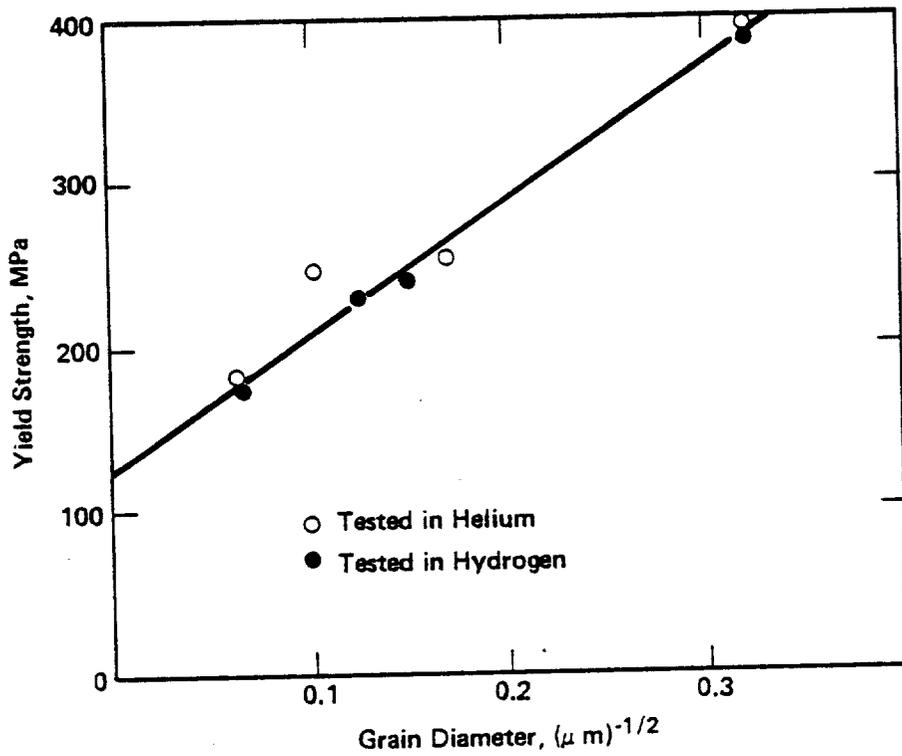
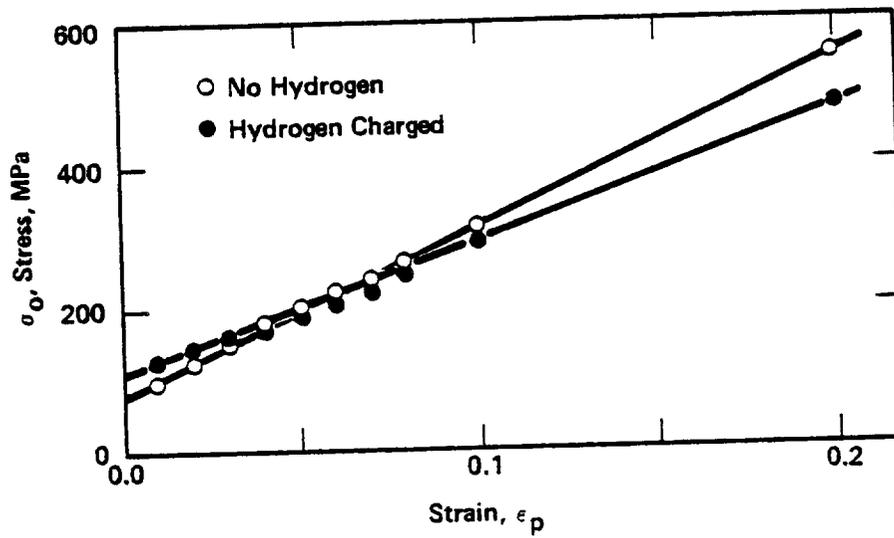
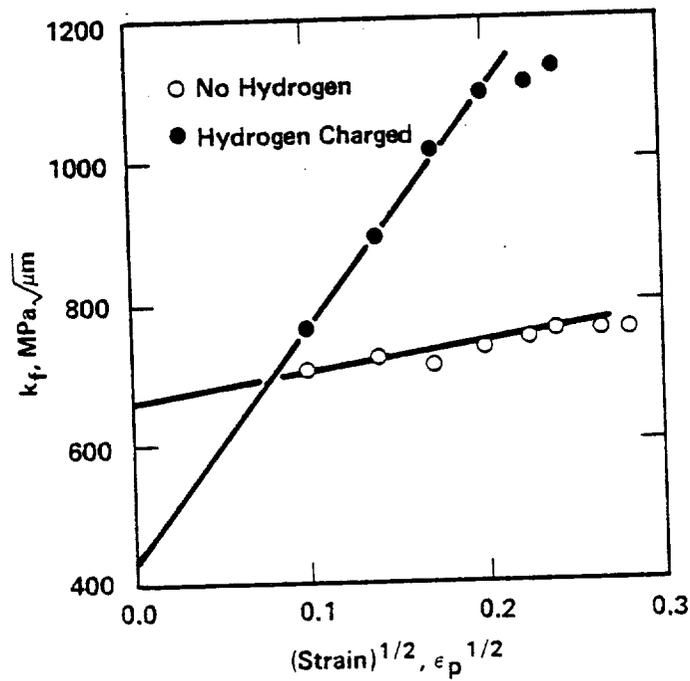


FIGURE 3. Hall-Petch Plot of Yield Strength for Type 304L Stainless Steel Tested in High-Pressure Helium or Hydrogen Environments



4a. Strain,  $\epsilon_p$



4b.  $k_f$

FIGURE 4. Strain Dependence of Hall-Petch Parameters

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